



31761 04213 4809

Gerstein Science Information Centre

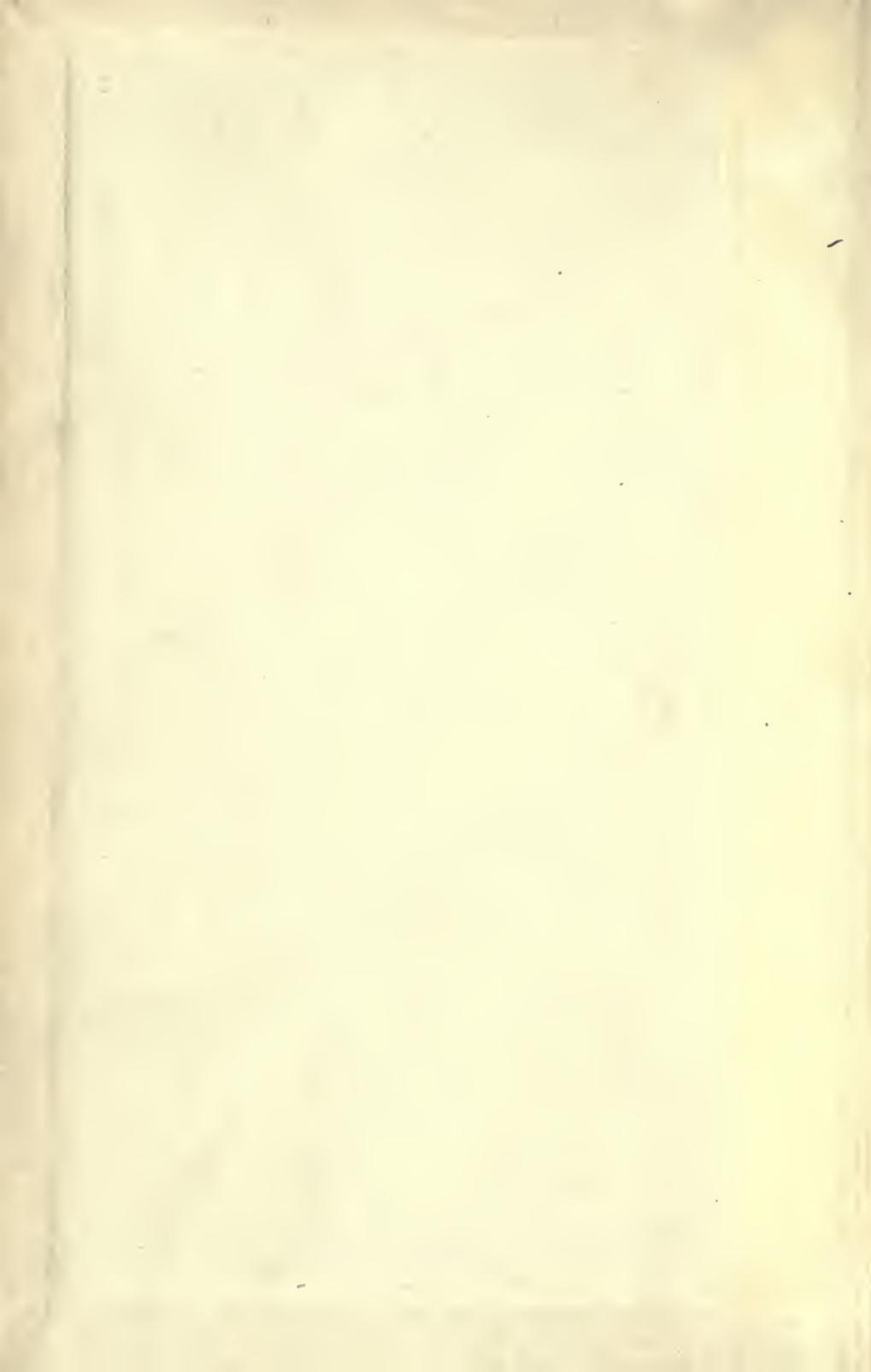
This volume is damaged or brittle
and CANNOT be repaired

Handle with **extreme care**:

- photocopy only if necessary
- return to staff
- do not put in bookdrops

OLD
CLASS
C
R3884 k x
c. 1
PASC

UNIV. OF
TORONTO
LIBRARY





Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

C
R8884kx

THE
Royal INSTITUTE OF CHEMISTRY
OF
GREAT BRITAIN AND IRELAND.

FOUNDED, 1877.

INCORPORATED BY ROYAL CHARTER, 1885.

[Lectures]. [No 1-5]

LECTURES

ON

CEMENT.

BY BERTRAM BLOUNT, F.I.C.



12263
18/6/12

30, BLOOMSBURY SQUARE, LONDON, W.C.

1912.

*The Lectures were delivered before the Institute
of Chemistry, at King's College, London, on
October 26th, and December 1st, 1911.*

CONTENTS.

	PAGE
Syllabus	4
Lecture I.: Cement	5
Lecture II.: Portland Cement	26
Appendix A: Analyses of Portland Cement and Cement Raw Materials	48—49
Appendix B: Methods of Analysis	50
Appendix C: Method of Preparing Cement from Raw Materials on an Experimental Scale	58
Appendix D: Significant Clauses of the British Standard Specification for Portland Cement	59

ILLUSTRATIONS.

Engineering Standards Committee Apparatus for conducting the "Le Chatelier" Test	63
Experimental Furnace for making Cement	64
Sampler	65
Tensile Testing Machines	66—67
Diagrammatic Plan of the Process of Manufacture.	

SYLLABUS.

General meaning of the term and its limitation in the present discourse. The principal structural cements will be dealt with, and minor adhesives of the workshop will be touched on only incidentally and illustratively, if at all. In practice this delimits the term to calcareous cements.

Historical account of the evolution of cements in this limited sense. Cement making is a branch of chemical manufacture.

Chemical reactions and physical changes involved in the production of cements and in their setting and decay.

Modes of testing, both chemical and physical, the latter including mechanical tests as ordinarily understood. Standardisation of all tests which from their nature are arbitrary, and the device and acceptance of standard specifications. The British Standard Specification as an example.

The uses of cements and the errors which may occur from unintelligent application.

The causes of failure of structures made with cement.

The importance of the aggregate used with cement to make mortar and concrete, and the errors which arise from want of knowledge of its properties.

The necessary equipment of knowledge and training for an expert. Physical and mechanical knowledge an essential, in addition to ordinary chemical training.

The ignorance now existing of the constitution of cement as produced and when set; the admirable but insufficient work of the past and the consequent opportunities for rigorous research in a subject of exceptional difficulty.

Lecture I.

CEMENT.

In its ordinary acceptation, putting etymology aside, the word "cement" means a material capable of sticking things together, and includes such entities as glue, rust and blood in its literal and racial sense. In practice and with respect to matter only, calcareous cements are of such predominant importance, that "cement" without epithet or context commonly and by custom connotes a binding material which has lime as an essential constituent, and it is this limited use of the word which I shall adopt in the present discourse.

The earliest form of calcareous cement is probably calcium sulphate sufficiently dehydrated to form plaster of Paris. Its merit as a cement is not great, as it lacks plasticity and expands considerably in setting. It is, moreover, easily attackable by water. Its mode of setting, however, by successive hydration in such a way that a small quantity of water, insufficient for the crystallisation of the mass at a stroke, is ample for the crystallisation of the mass step by step has, as the result of much study, thrown such light on the probable mechanism of hydration of calcareous cements proper that plaster of Paris cannot be dismissed altogether from consideration as a cement, and I shall use it as an illustration when I come to discuss the reactions which are believed to occur in the setting of cements of greater importance.

Although no exact record exists, it may be reasonably

surmised that the accidental burning of some form of calcium carbonate put into the hands of a primitive and curious architect a substance which he perceived to have merit as a structural material, and that such casual observation was the origin of our present knowledge of calcareous cements and of the industry concerned in their production.

In times previous to the discovery of lime and in countries destitute of its carbonate, any clayey material which was sufficiently plastic to be spread and to fill interstices and was capable of becoming hard when dry, was no doubt freely used as a cement. The advantage over such material possessed by lime lies in the fact that whilst similarly plastic and similarly capable of hardening, the hardened material has a greater resistance to moisture than is exhibited by any argillaceous substance. That this resistance is due either to absorption of carbonic acid from the air or to the hydration of siliceous compounds, or to both, was of course unknown to the ancient users of lime, but their appreciation of the fact is evident from the universal employment of some form of calcareous cement from almost prehistoric times. It would be difficult to find any substance other than lime having these necessary qualities, except, perhaps, the other alkali earths and, in a minor degree, magnesia. Strontia and baryta can be made into fairly plastic masses with water and will harden on drying and by absorption of CO₂, but their relative scarcity puts their use out of the question. Magnesia is more abundant, but gives a mass which is less smooth and plastic than lime and sets sometimes well and sometimes ill. I have prepared many specimens of magnesia from various supplies of magnesite with a view to their use as a true cement—for magnesia, unlike lime, will “set” in the manner of cement—but the product is anomalous and in practice difficult to obtain of uniform quality. Broadly stated, it seems that magnesia lightly burnt, say at about 900° C., will hydrate and will set

when kept moist, but is mechanically weak, and that no great difference in behaviour occurs when a higher temperature is used. A true cementitious material may be easy to obtain, but my own success in attempting its production is insignificant. The statements in the text-books are not to be taken too seriously, and the matter is one eminently suitable for enquiry. There is an industrial side to the question, as a white cement capable of standing occasional but heavy rain, and by its whiteness warding off the sun, would be acceptable in some tropical countries, and I commend this view of the matter to the investigator.

Lime by itself is an imperfect cement. In drying, the paste made by gauging lime with water shrinks so greatly that some inert diluting substance must be added in order that it may form a satisfactory mortar. The notion of an added substance being useful is found in the "Rejected Addresses" of James and Horace Smith,* where we find these moving words :—

"I sing how casual bricks, in airy climb,
Encountered casual cow-hair, casual lime ;
How rafters, borne through wondering clouds elate,
Kissed in their slope blue elemental slate,
Clasped solid beams in chance-directed fury,
And gave to birth our renovated Drury."

As far as I know "casual cow-hair" no longer encounters "casual lime," but its use is apparent when it is considered that, until carbonated, lime mortar has but little more coherence than so much dried mud. The curious thing is that a nitrogenous material like cow-hair, easily influenced by a powerful alkaline substance like lime, should have been chosen as the mechanical bonding material; the ease with which porous lime mortar dries may account for the stability of the organic bond.

* "Architectural Atoms."

It was long supposed that the setting of lime mortar is due to the action of lime on the sand with which it is mixed. The limited truth and substantial error of this belief are good illustrations of the need, constantly neglected, of defining one's terms. For example and in this instance, what is meant by sand? If clean quartz sand is meant, then it may be confidently said that at the ordinary temperature lime will have no action upon it except in the sense that conceivably two substances capable of reacting at a higher temperature may tend towards the same reaction at a lower temperature if unlimited time is allowed. But if a sand containing hydrated silica or decomposable silicates is referred to, then it is possible enough that union will occur between the lime and the silica thus provided. Substantially, however, the action of lime on sand in mortar is negligible. The reason for the contrary belief is that analysis of old mortar has disclosed the presence of combined silica, whereupon the analyst has jumped to the conclusion that the silica came from the quartz composing the bulk of the sand. As a matter of fact it came chiefly from the silicates associated with the carbonate of lime from which the lime had been prepared, or in minor degree from hydrated silica or attackable silicates in the sand which in process of time had combined with the lime.

By a fortunate accident calcium carbonate rarely occurs pure in nature. Putting aside such substances as perfect crystals of calcite and Iceland spar, it may be safely said that all native calcium carbonate contains impurities. I include the purest procurable white marble in this statement. It is also fortunate that frequently the impurities are siliceous. (Sometimes it is true the impurity is magnesia, but even then the accident is fortunate because dolomitic limes set *per se.*) So it comes about that when impure calcium carbonate of this kind (*i.e.* siliceous) is burnt, there is every opportunity for the

resulting lime to act as a base on the silicates present and to form calcium silicates and aluminates. The analogy between carbon and silicon—always imperfect—is entirely wanting in this instance, for the cementing product of the action of CO_2 on CaO , *i.e.* CaCO_3 , is not reproduced in the action of SiO_2 on CaO . Wollastonite, CaSiO_3 , may certainly be formed by the action of lime on silica, but its value as a cementing material is *nil* and more basic silicates play that rôle.

It was said above that silica and lime do not interact at the ordinary temperature within periods less than geological. But above that temperature interaction occurs. I have not determined at what point the action becomes appreciable, but I have found that at $150^\circ \text{C}.$, in the presence of water, lime and quartz sand combine and a cementitious silicate is formed. It is on this chemical fact that the manufacture of so-called lime-sand bricks depends.

The fact that the impurities in limestones, chalks and marls are usually siliceous causes lime made from these substances, while retaining in a fair degree the plasticity of pure lime, to have the capability of setting in a cementitious sense, in distinction from becoming hardened by absorption of CO_2 . On this account it has often happened that limestones containing silica have been used not by prescience on the part of the builder, but because they were locally procurable. The stability of structures made with such material has been due to luck rather than thought, and any argument based on it to the effect that ancient buildings now existing have been well contrived rests upon an amiable illusion.

It seems that after it was understood empirically that some limestones are better than others in providing strong and resistant lime for mortar, the advantage of some siliceous materials over others as the aggregate of mortar was observed. When common lime is used as a binding material, sand containing hydrated silica or attackable silicates is better than

quartz sand, and pozzolana is better than either. In volcanic countries there is abundance of such substances having local and trivial names—trass, santorin earth, tufa, and the like—having similar composition and identical function. Originally these were used simply as so much sand or other diluting material in which case the coarse parts would serve for that purpose, and the finer would unite chemically with the lime. In later practice the whole of the pozzolanic material is finely ground so as to fulfil the latter office and inert aggregate is provided for the mixed lime and pozzolana. If the mortar is prepared at the place of origin, it is usual to let the pozzolana act as aggregate as well as a cementing material. It may be added that such artificial pozzolanas as granulated blast furnace slag, burnt clay and furnace ashes are often used, and, if well chosen, form excellent cements when mixed with ordinary lime. The following are analyses of various forms of pozzolana :—

	Roman.	Neapolitan.	Java Trass.	Granulated Blast Fur- nace Slag.
	%	%	%	%
Soluble silica (SiO_2)	32·64	27·80	19·32	26·34
Insoluble siliceous residue ...	25·94	35·38	50·40	0·30
Alumina (Al_2O_3)	22·74	19·80	13·86	18·71
Ferric oxide (Fe_2O_3)	—	—	—	0·95
Manganous oxide (MnO)	—	—	—	0·08
Lime (CaO)	4·06	5·68	3·10	45·90
Magnesia (MgO)	1·37	0·35	0·13	5·07
Sulphur (S)	—	—	—	1·00
Sulphuric anhydride (SO_3) ...	trace	trace	trace	0·76
Combined water and carbonic anhydride (CO_2)	8·92	4·27	7·57	0·96
Moisture, alkalies and loss ...	4·33	6·72	5·62	—

The amount of soluble silica serves as an index of the cementitious value of these substances, but it would be incorrect to say that the indications are absolute ; it is not even known whether the silica called "soluble" and extracted by different analytical methods has the same cementitious

value, and it is more than likely that not only the soluble silica, but a portion of the silicates is capable of uniting slowly with lime; hence the appraisement of the quality of a pozzolana should include the determination of the mechanical strength of test pieces made from a mortar prepared from it, lime and a suitable aggregate.

Up to this point I have spoken of those calcareous cements which have long been known, and have drawn no distinction between aerial and hydraulic cement. The builders of antiquity soon observed that whereas mortar made from pure lime would not resist the action of water sufficiently to withstand immersion, yet when the limestone was siliceous, or was mixed with siliceous material, such as pozzolana, it was resistant in this sense—formed as we now say an hydraulic cement. I do not find any record that limestones were deliberately and intelligently chosen for the hydraulic quality of the lime which they furnish until the time of Smeaton, who in considering with what material he should build the Eddystone Lighthouse, ascertained that Aberthaw limestone (a blue lias formation) was undoubtedly hydraulic, and, desiring to know why, applied to Mr. Cookworthy, a chemist of the period whose office as a consultant was creditably fulfilled. It was found that those limestones which were most hydraulic contained the largest proportion of argillaceous matter. But not content with this, he reasoned that this quality might be improved by the addition of what was then known to be capable of conferring hydraulic properties on ordinary lime, and accordingly used Trass. In his own words :—

“ In this respite from sea operations, I seriously began to consider the great importance that it was likely to be of to our work, to have a *Cement* the most perfect that was possible, to resist the extreme violence of the sea. And on a consideration of this matter, it appeared, that nothing of the

resinous, or oily kind, could have any place in our work, as it would require the surface to be *dry*, to enable it to make a compleat adhesion ; whereas the getting anything *completely dry*, was one of our greatest difficulties. It seemed, therefore, that nothing in the way of Cement would answer our end, but what would adhere to a moist surface, and become *hard*, without ever becoming completely *dry*.

"I began now to foresee that before I could have a compleat sample produced of every part of the work, that might be wanted for the operations of next season, it would be pretty far advanced in the spring ; and as I proposed beginning the outwork as early in the season as possible, I determined to winter at Plymouth (without returning to my residence in London, as I had before intended) though to the detriment of my own private concerns ; laying every consideration aside in favour of the Edystone. I therefore resolved to take every opportunity in the evenings and intervals of my attendance on the work-yard, mould-room, etc., to go through a compleat set of experiments on *Cements*, so far as it concerned the subject I had in hand ; for I plainly saw from the manner of working the moorstone, already described, that not only much of the beauty and neatness of the work, but its real solidity too, would depend upon getting a Cement that would, in despite of water almost continually driven against it with every degree of violence, become of so firm a consistence in itself, and adhesion to the stone, that it should lie fair and flush in the joints, and so as to compose one even regular surface with the stone ; and without needing *hoops of iron or copper* to surround the horizontal joints, as seems to have been the expedient of Mr. Winstanley. I was so fortunate as to succeed in this part of the business entirely to my satisfaction ; and perhaps in a degree unknown before ; and having made much use since of the experience which I then acquired ; having had frequent occasions and

opportunities of communicating it to others, and having been asked many questions concerning it; I trust that my reader will forgive me, if I am diffuse enough to enter into a full explanation of the subject, so far as I know it. I mean not however to tire him with recording all the particular experiments, as this would be almost endless, they having been pursued through the whole of this winter; but only to state the principal scope and design of them, with the results; nor do I propose to enter into a chemical disquisition upon them, which I leave to the learned in that science. But as what I have to say on this subject will carry me to some length, I shall reserve it to a distinct chapter, in order to keep the matter together.

"On this subject I was already apprised that two measures of quenched or slaked lime, in the dry powder, mixed with one measure of *Dutch Tarras*, and both very well beat together to the consistence of a paste, using as little water as possible, was the common composition, generally used in the construction of the best water-works both in stone and brick, and which, after being once set,* would afterwards become hard, without ever being compleatly dry; nay, that it would in time grow hard, even *under* water. This therefore seemed to be the kind of cement adapted to our use.

"Having heard of a lime produced from a stone found at Aberthaw, upon the coast of Glamorganshire, that had the same qualities of setting in water as *Tarras*, I was very anxious to procure some of the stone, which I did, and burnt it into lime. I found it to require a good deal of fire to make it, by quenching, fall into a fine powder. This stone, before burning, was of a very even, but dead sky blue, with very few shining particles; but when burnt and sifted, it was of a

* "This is the term used in the application of calcareous mortar, which denotes its first step, or degree of hardening; but in this state, though it has lost its ductility, it is a very friable substance."

bright *buff colour*. Having made up a couple of balls, according to each of the former proportions ; and also a couple of balls with common lime (by which I mean Plymouth lime) the difference of hardness after twenty-four hours was very remarkable : the composition of two measures of *Aberthaw* to one of *Tarras* considerably exceeded in hardness that of common lime and *Tarras* in equal parts ; the composition of Aberthaw and *Tarras* in equal parts was still considerably harder, and this difference was the more apparent the longer the compositions were kept.

“ Having now found a species of materials, and a method of compounding them very competent to our purpose ; and having plainly seen that there was a great difference in the effect, arising from the different *nature* of lime burnt from different kinds of limestone ; and that its acquisition of hardness under water did not depend upon the hardness of the stone ; inasmuch as *chalk* lime appeared to be as good as that burnt from *Plymouth* marble ; and that Aberthaw lime was greatly superior to either for the purpose of aquatic buildings, though scarcely so hard as Plymouth marble ; I was very desirous to get some light into some of the *sensible* qualities, that might probably occasion the difference, or at least become a *mark* of distinction. I therefore applied to my friend Mr. Cookworthy, whom I had found at all times ready to afford me his assistance, wherever his knowledge could be of use to me. He taught me how to *analyse* limestones : and though my *chemical* friends will be at no loss upon this subject ; yet as it is very possible that some of my readers may be no more acquainted with chemistry than myself ; for the sake of these I will describe the process, as being useful for all those who are concerned in building to know.

“ I took about the quantity of five penny weights (or a *guinea's weight*) of the limestone to be tried, bruised to a coarse powder ; upon which I poured common aqua fortis, but

not so much at a time as to occasion the effervescence to over-top the glass vessel in which the limestone was put; and added fresh aqua fortis after the effervescence of the former quantity had ceased, till no further ebullition appeared, by any addition of the *acid*. This done, and the whole being left to settle, the liquor will generally acquire a tinge of some transparent colour; and if from the solution little or no sediment drops, it may be accounted a *pure* limestone (which is generally the case with white *Chalk* and several others) as containing no uncalcereous matter; but if from the solution a quantity of matter is deposited in the form of mud, this indicates a quantity of uncalcereous matter in its composition. When this is well settled, pour off the water, and repeatedly add water in the same way, stirring it and letting it settle till it becomes tasteless. After this let the mud be well stirred into the water, and without giving it time to settle, pour off the muddy water into another vessel: and if there is any sand or gritty matter left behind (as will frequently be the case) this collected by itself will ascertain the quantity and species of sabulous matter that entered into the texture of the limestone. Letting now the muddy liquor settle, and, pouring off the water till no more can be got without an admixture of mud, leave the rest to dry; which, when it comes to the consistence of clay, or paste, make it into a ball and dry it for farther examination.

“ From the experiments now related, I was convinced that the most *pure* limestone was not the best for making mortar, especially for building in water: and this brought to my mind a maxim I had learnt from workmen; that the best lime for the *Land* was seldom the best for *Building* purposes; of which the reason now appeared; which was, that the most pure lime affording the greatest quantity of *Lime Salts*, or impregnation, would best answer the purposes of *Agriculture*: whereas, for some reason or other, when a limestone is intimately

mixed with a proportion of *Clay*, which by burning is converted into *Brick*, it is made to act more strongly as a Cement.* This suggested to me the idea, that an admixture of Clay in the composition of limestone, when treated as above specified, might be the most certain index of the validity of a limestone for *Aquatic Buildings*: nor has any experience since contradicted it; as all the limestones in repute for water-works, that I have met with, have afforded this mark; even the *Dorking* lime much esteemed for these uses at *London*, and in the country round about, is plainly nothing but a species of chalk, impregnated with clay, of which it makes one full seventeenth part of the original weight."

The manufacture of hydraulic lime from such materials as blue lias limestone which contains much alumina and from those like the limestone from Teil which is almost free from alumina but is rich in silica finely divided and evenly distributed continued to be the chief source of hydraulic cement other than that prepared with pozzolana until 1796, when "Roman cement" began to be made. Roman cement is named on the principle used for its supplanter, Portland cement. It has as much to do with Rome as Portland cement has to do with the various Portlands which sprinkle the world. True Roman cement is a mixture of lime and pozzolana; the substance called "Roman cement" is a crude form of Portland cement made by burning lumps of clayey limestone which are hard enough to persist when their matrix is broken up by water and remain as dredgable nodules in

* "It is not to be wondered at, that workmen generally prefer the more *pure* limes for building in the *Air*, because being unmixed with any uncalcareous matter, they fall into the finest powder, and make the finest paste, which will of course receive the greatest quantity of *Sand* (generally the cheaper material) into its composition, without losing its toughness beyond a certain degree, and requires the least *labour* to bring it to the desired consistence: hence mortar made of such lime, is the least expensive, and in *dry work* the difference of hardness, compared with others, is less apparent."

various estuaries. The following analysis will give an idea of its nature, and for convenience one of blue lias lime is put beside it :—

	Roman Cement.	Blue Lias Lime.
	%	%
Insoluble siliceous matter 5·86	... 2·39
Silica (SiO_2) 19·62	... 14·17
Alumina (Al_2O_3) 10·30	... 6·79
Ferric oxide (Fe_2O_3) 7·44	... 2·34
Manganous oxide (MnO) 1·57	... —
Lime (CaO) 44·54	... 63·43
Magnesia (MgO) 2·92	... 1·54
Sulphuric anhydride (SO_3)	... 2·61	... 1·63
Carbonic anhydride (CO_2)	... 3·43	... 3·64
Water (H_2O) 0·25	... 2·69
Alkalies and loss 1·46	... 1·38

Slowly and empirically the manufacture of Portland cement began. I decline to go through the phases of its history, the more because some of its progenitors may be still alive. Suffice it that starting with the notion of imitating Roman cement, they arrived at the idea that when chalk and clay were mixed and burned, an hydraulic material was produced. I believe it is in the books that in the beginning of the industry all good clinker was rejected. Much the same thing happened in France where those particles which remained unaffected by water when chaux de Teil is slaked were at one time rejected. This unslakable part includes unburnt limestone and any portions of matter so siliceous as to form an acid or neutral silicate with the lime, and of course these are usefully removed. But it also includes particles which, unlike the mass of the Teil lime, contain sufficient alumina to cause them to sinter at the temperature of the kiln. They form, in fact, masses of true clinker, inert in the lump, but yielding admirable cement of the Portland class.

At the time when in a blundering and empirical manner a sort of spurious "Roman" cement was being prepared with care to discard all the best parts, no one suspected that the foundations were being laid for one of the hugest chemical

industries in the world. At the present date the world's yearly production of Portland cement is about 25,000,000 tons, having a value of some £35,000,000.

The state of knowledge of some cement makers at the inception of the industry and long afterwards is illustrated by a fact within my own memory. A very noted and justly esteemed managing director of an important and most remunerative works assured me not casually or once, but earnestly and repeatedly, that he sought only mechanical union of his chalk and clay; the burning was a ceremony likely to bring this about; any chemical action was a chimera, unworthy of the brain of a practical person. With the rashness of youth I tried to convince him of error, and earned his respect for my courage at the expense of his regret for my presumptuous ignorance.

Excellent descriptions can be found in many accessible books and papers of the mode of manufacturing cement now in use, and I do not propose to enter into the technology of the subject, but to content myself with saying that the essence of the matter is to cause the interaction of argillaceous and calcareous materials at such a temperature and in such proportions as to form a clinker which, when ground, will set and be strong and remain sound.

In like manner it is not my intention to describe many varieties of cement of the Portland class which can be prepared, such as so-called "natural" cement made from marl or rock of approximately similar composition to that of an artificial mixture of chalk and clay, and cements made from blast furnace slag and limestone. Although of importance locally, they are of small significance when compared with Portland cement proper, and nearly all that may be said of that will be relevant to them.

We now come to the function of the chemist who concerns himself with this great chemical industry.

When a new works is to be started it is necessary to consider the nature and the available quantity of the raw materials, the accessibility of a supply of fuel, the suitability of the site for the required buildings, the choice of process and the appropriate plant and such matters as transport, supply of labour and probable markets which go far to determine the commercial success of any undertaking. Of these data the quality of the raw materials is obviously a question for the chemist, but as the modern consulting chemist would be poorly equipped if his knowledge were confined to his laboratory it often happens that he is called upon to advise more widely and according to his knowledge of things mechanical and manufacturing, he may, either alone or in conjunction with an engineer, settle the whole matter. For such a task good ordinary sense is at least as important as technical knowledge, for special information can always be obtained from special sources, but common sense is either native or absent.

For our immediate purpose, in considering the function of the chemist I will confine myself to what is obviously chemical, that is, the examination of the raw materials, and at the outset will say that proper sampling of these at the sites is of primary importance. In cases where cement works are already established on deposits of similar character, it is evident that existing information regarding their quality will save much labour, but on a new site where only some geological data are available and those often far from complete, a rigorous investigation is absolutely indispensable. The uniformity or variety of the material must be ascertained by taking samples in number proportional to the amount of variation suspected; these samples must be of generous dimensions, and must be examined either partially or fully according to the variation. Sometimes a number of partial analyses will disclose the comforting fact that the whole deposit is practically homogeneous; sometimes it will happen that a regular alteration

of composition can be traced, and, worst case of all, occasionally the difficulty has to be faced of dealing with material "patchy" in character. After the composition of the raw materials has been ascertained, it is necessary to determine whether they can readily be made into cement; and no analysis, however exact, chemically or mechanically, will be definitive. A valid opinion can generally be arrived at, but the ultimate test is the preparation of cement of quality not merely tolerable, but equal to the accepted standard. It follows that the raw materials in the proportions indicated by analysis shall be mixed and burned together *imprimis* in some simple furnace such as can be rigged up in any decently-equipped laboratory, and if the question is doubtful, in a full-sized kiln under practical conditions of manufacture. Should the materials be in any way abnormal, whether calcareous or argillaceous, the necessity is more pressing, and if the fuel be abnormal the question of its best mode of use and its influence not only on the ultimate composition of the cement, but also on the mode and conduct of the burning, will become imperative. The result of this enquiry will, in the first place, decide whether the deposits are of so difficult a character that to manufacture cement from them would be a fruitless if possible task, and in the contrary case to lay down for the coming works' manager a plan showing the pitfalls into which his raw materials may lead him, and in the last and best event to assure him that his materials are so good that it is useless to ascribe his failures and difficulties to them. As regards the mode of examination of the samples, it may be said that though the methods of chemical and mechanical analysis employed involve nothing but principles generally known, yet there are a few points which need special attention; and for convenience, and not to cumber this lecture with detailed descriptions of laboratory operations, I have relegated all such matters to an appendix in which will be found these modes of

examination which, according to my experience, are both accurate and convenient.

Assuming our supposed new works to be started, the function of the chemist continues though on rather different lines. Sometimes the consultant who advised originally on the raw materials and on such other matters as he was competent to deal with, may be retained for the benefit of his knowledge and experience when difficulties other than those commonly occurring in the routine running of a works arise, or in the event of litigation being necessary. Sometimes he passes out of the picture, to re-enter it only when the trouble has begun or has become acute. In either case his function is well defined ; he is a resource in difficulties greater than those of daily happening and an adviser on what is new ; in addition, he may occasionally visit a works and confer with the resident chemist and aid him in making certain that all the operations of the works' laboratory are conducted according to the latest scientific knowledge and are efficiently carried out. But it is on the resident chemist that the smooth control of the composition of the cement depends, and unless the raw materials are exceptionally uniform, his task is one requiring constant vigilance and much hard work. His laboratory should be thoroughly equipped with good appliances to save labour and to make for ease of manipulation. He should not be stinted in manual help, and although it is right that he should know well how to make mechanical tests and to be able if necessary to perform these himself, yet the work of mechanical testing should not be expected of him, but obtained from a good gauger working under his supervision. I am speaking, of course, of a works' chemist as a unit. In a large works a considerable staff will be necessary, as in any other chemical manufacture.

In addition to determining the composition of the raw materials and of the cement, and making such alterations in

the proportions of the latter as will compensate for any fluctuation in their quality and will ensure a uniform and normal composition of the cement made from them, the resident chemist must be prepared to analyse and test calorimetrically the fuel which is used in the works, that fuel including coal, probably both steam and slack, coke too, possibly, liquid fuel, whether for kilns or Diesel engines it may be, and producer gas in the case where internal combustion motors are employed. Ordinary engineering stores such as oils and paints, water, and structural materials such as other people's cements when his own firm's runs short, or is better sold than used, will also come within his purview. These latter materials will require from him general chemical knowledge such as it is the aim of the Institute of Chemistry to ensure to its members, but as regards his raw materials and the cement made from them he should have a more special knowledge and the readiness and skill proper to the specialist in any branch of work.

In a subsequent lecture I hope to deal in some detail with the chemistry, properly so called, of cement. In this it is sufficient to indicate the chief chemical changes which occur in the production of the material. In the Appendix are tables of analyses of some of the more usual raw materials such as chalk, clay, limestone, shale, "cement rock" as it is termed, and marl. In all cases the composition and proportions of these must be so adjusted that Portland cement of composition such as is given in the Appendix shall be prepared. Choice of the proportions involves a simple calculation, and it may be noted in passing that though a respect for the proprieties demands the use of algebraical symbols, much the simplest way when one or two such calculations have been made and a little experience has been gained, is to say by inspection what is a likely proportion and to find what composition of cement this proportion represents—the barbarous

process of trial and error for once saving time and avoiding blunders. However arrived at by adjustment of the less and the more calcareous of the materials, there will be found in the dry mixture lime equivalent to about 75 per cent. of CaCO_3 and the balance, 25 per cent., composed of silica and alumina + oxide of iron, in the proportion of about two of silica to one of alumina and oxide of iron jointly, and some combined water with such minor constituents as magnesia, sulphur as sulphides and sulphates, and alkalies.

When the adjustment by calculation from the analyses has been completed, the correctness of the result will be checked by direct experiment conducted in the same way as that previously indicated, *i.e.*, by a direct burning trial, and here the resident chemist is at a great advantage because the plant at his works will allow him to make experiments on a scale far larger than can be obtained by his adviser, unless the latter is fortunate enough to obtain the temporary use of a plant. But as the interruption of regular manufacture for the purpose of experiment, however ultimately fruitful, is temporarily inconvenient, it is best in the first instance to make small burning tests by the simplest methods. Any form of furnace capable of heating raw materials to a point where they clinker and without contamination with the materials of the furnace walls will suffice, provided that the quantity of clinker produced is sufficient to prepare cement adequate for the usual mechanical tests.

When the raw material enters the upper end of a rotatory kiln, the first change is the expulsion of free water which may be in trifling amount when the dry process is used, and may be as much as half the weight of the slurry when the wet method is used. The material thus dried passes down the kiln, loses combined water and CO_2 and is raised to such a temperature that the lime begins to interact with the silica and those oxides like alumina and ferric oxide capable of

playing the part of an acid, with the result that calcium silicates, aluminates, and the like, are found, chiefly of a basic character. The preponderance of base is sufficient to prevent the mass fusing even at the high temperature (about $1,400^{\circ}$ C.) obtaining in the fire-zone of the kiln, but an incipient fusion or clinkering occurs so that the heated material is no longer a powder but is agglomerated into hard masses varying from the size of a pea to that of a walnut, though sometimes such pieces may ball together and form lumps as big as a medium-sized melon. This stage of clinkering is essential to the production of sound cement, as even with the most careful grinding the basic and acid constituents are still present as particles of very appreciable size—some of them, say, $\frac{1}{270}$ in. in diameter—and these must have opportunity to unite, an opportunity not properly afforded unless the medium is at least plastic. So little was this understood in former days, that one of the best early attempts to use a continuous rotatory process for cement manufacture largely based its claim for consideration on the assumption that a fine powder fed in at one end would emerge as an equally fine powder after it had been burnt, and thus would need no grinding. Far from this being the case, the burnt material is not only agglomerated, but also the agglomerations are hard and tough, and useless as cement until ground. Even when ground and mixed with water the hydration necessary for their setting and acting as a cement takes place only partially. Naturally there is no hard and fast line to be drawn between particles which are small enough to become hydrated and those which are too large, as evidently even the largest must suffer hydration to the surface. This surface in relation to the weight of the particle is too small for effective attack with any but almost impalpable particles, and it may safely be said that no particles which fail to pass a 180×180 mesh sieve, *i.e.*, have a mean diameter greater than 0.004 in., have any cementitious value, and that many of

those which do pass are still too coarse to become properly hydrated by the water. Thus it comes about that just as most careful comminution of the raw materials is needed to allow them to unite with each other, so equally a like painstaking pulverisation is necessary to enable the product to enter into the reactions which change dry powdered clinker into set cement.

Assuming, then, that the raw materials have been well chosen, have been used in the right proportions, and have been so finely ground that the substances whose union is required will be close enough together in the sticky mass of clinker to be able to combine ; that the desired composition has not been disturbed by the incorporation of too much or too little of the siliceous ash of the fuel and that what has been incorporated is evenly distributed ; that the temperature has been high enough for complete clinkering and not so high as either to fuse a normal clinker or to cause it to attack the acid lining of the kiln ; that the clinker thus obtained has been properly quenched or stored ; that it is not so difficult to grind as to give a coarse product when the mills are turning out their proper quantum ; that the setting time has shown none of those fantastic variations to which the best-regulated cement is heir :—then, assuming all this, may the resident chemist consider his duty to have been accomplished, and leave in other hands such trivial matters as controlling; coercing or cajoling troublesome plant, insurgent men and coy consumers.

Lecture II.

PORLAND CEMENT.

In the first lecture we had reached a point where the consulting and resident chemist had jointly arrived at so satisfactory a mode of procedure that nothing remained for the manufacturer engaging their activities but to attend to his proper business of providing adequate management at his works and at his distributing office. But before he is in a position to ensure that the commodity he makes is saleable, he must be prepared to entrust it to cold critics who care nothing about the perfection of his management or the views of his technical staff or advisers, but are most pertinently intent on the quality of the cement which all this human machinery has provided. So callous are such persons that the most conscientious cement maker may come with tears in his eyes and test sheets in his hands indicating the impeccable character of his product and encounter a scepticism verging on the brutal, which will say that whatever merits the cement may possess it must pass certain standard tests.

A history of methods of testing cement would be of interest, but only of minor and recording interest. It differs in that respect from the history of cement itself, as that concerns the evolution of a chemical industry involving a study of the nature of the material sought, whereas a history of testing would be merely a record of rather empirical efforts to appraise in some way the quality of the material. Because of

our limited knowledge of the chemistry of cement, it is impossible to make this valuation by any strictly scientific methods, and thus it comes about that tests which have been proposed and used are always, from their origin, arbitrary, and must include the determination of physical and mechanical criteria as well as those purely chemical.

I do not intend to describe the crude but sensible methods of testing which older experimenters employed, but will go at once to the modes of testing used to-day. They comprise the determination of certain chemical, physical and mechanical data, each non-decisive in itself, but conclusive when considered as a whole. This mode of determining the quality of structural materials is quite general, and the advocates of any particular method of testing, we will say, so important a structural material as steel, are in error when they base their opinion on any single criterion, however good.

This fact has been recognised for many years by those concerned with drawing up specifications for testing cement, and was held steadily in view when the British Standard Specification was constructed. The committee responsible for this document included engineers and contractors, chemists, architects and manufacturers and representatives of those official bodies whose public works require large quantities of Portland cement which should be dependable in every sense. As the result of their labours a document was prepared in 1904, which so nearly embodied the knowledge and requirements of the time that except for modifications tending to improve the quality of the cement supplied under the specification made at suitable intervals, the British Standard Specification of to-day is in essence identical with that originally drafted.

It includes the chemical analysis of the cement by which its ultimate composition is determined and prescribed to lie between limits set by the basicity and acidity of its

component oxides, and found practically attainable by manufacturing experience; the mechanical strength of cement when tested by itself and when mixed with a defined proportion of sand of a defined quality; the specific gravity of the cement to exclude such materials as are underburnt; the constancy of volume of cement—it being understood that alteration of volume by alteration of temperature alone is not considered—in order to exclude all stresses other than those proper to the structure as distinct from the material of that structure; the degree of comminution to ensure that what is bought shall be capable of hydration, and shall not include matters so coarse as to be practically inert; the time of setting chosen according to that necessary for mixing and handling the cement together with the materials which it is to cement.

It may be of some interest to consider the recognised modes of testing cement step by step, and in rather more detail than that proper to a sketch of the principles such as has just been given.

First, as regards fineness. The tendency for many years has been gradually to increase the severity of requirements in this direction. Whereas a residue of 10 per cent. on a sieve having $50 \times 50 = 2,500$ meshes per square inch was regarded with satisfaction some twenty years ago, at the present time not more than 18 per cent. on a sieve having $180 \times 180 = 32,400$ meshes per square inch is considered as erring rather on the side of leniency. The time of sifting is commonly prescribed, as it is easy to overestimate the amount of coarse material by failing to sift long enough to give all the fine particles an opportunity to pass the mesh, and it is quite possible by over-prolonged and diligent sifting to wear down some of the particles almost small enough to pass, and thus fall into the contrary error. The fineness of cement is one of the most important qualities to be determined as the coarser

parts are either practically worthless, or if the cement is slightly unsound may be a source of danger by belatedly hydrating and expanding.

The specific gravity is commonly determined, and is of value as indicating that the cement has been fully burned, and is free from such gross adulteration as would materially alter the specific gravity of a normal Portland Cement which is about 3.15. The values obtained must be interpreted with some care, as a perfectly well-burnt cement may have been slightly air-slaked by exposure and yet be in every way fit for use. When time or cost forbid the performance of a chemical analysis, the determination of the specific gravity is a useful sorting test, picking out those samples which by departing appreciably from the normal figure are proper objects of suspicion.

The determination of the chemical composition is of much use in two directions. In the first place, when the results are interpreted with intelligence, it allows of the certain detection of any kind of adulteration. It also shows whether the sample departs in any important degree from a composition, which by experience is known to be proper to a reliable cement. It does not follow that departure from the customary limits proves that the cement is bad, but, in the event of such departure, it becomes a matter of common prudence to scrutinise closely all the qualities of the sample before accepting it for service. As at present no means are known for the proximate analysis of cement, the user must be content with an accurate ultimate analysis. The ultimate analysis of a material containing as its chief constituents silica, alumina and lime, with small quantities of ferric oxide, magnesia, sulphuric anhydride and the like, presents no difficulty to any properly trained chemist, but as in practice, separation of these oxides must be done with fair speed and inexpugnable accuracy, it is useful to know what elaborations may be omitted, and what

precautions are indispensable. The method which I have found serviceable is given in the Appendix.

The mechanical strength of cement is of great importance, and many tests for its determination have been devised. All must necessarily be arbitrary and designed to represent in some degree the conditions obtaining in practice; therefore there has been a strong tendency, on the face of it reasonable, to use compressive tests as cement is not designedly used in tension. But as the chief utility of these mechanical tests is to afford a basis of comparison, it has been generally regarded as sufficient to make tensile tests of cement alone or of mixtures of sand and cement. Evidently in both cases it is necessary to prescribe the mode of mixing the proportions of cement, sand and water to be used, the size and shape of the test piece and such other working conditions which are not obvious to a commonsense operator, with the result that elaborate directions occupy much bulk in many specifications. Some such directions are requisite, but many are superfluous and ineffective, as a moderately competent worker does naturally what they prescribe, and a person determined to go wrong will always succeed.

In this and similar tests required for appraising the quality of cement, I regard the British Standard Specification as a model of the *via media*, not omitting due direction but assuming a modicum of gumption in its user. As that document is easily accessible I do not propose to do more than quote, as an appendix, those clauses which are of particular significance for our present purpose.

The setting time of cement can be determined with a fair degree of accuracy by methods necessarily arbitrary, because obviously there is no such thing as a true setting point. There is a point when the cement approaches rigidity, but, until the reactions involved in its hydration are complete, no finality in setting is possible. But again, in practice, it is

sufficient to adopt a simple apparatus such as the Vicat needle and to ordain that when that no longer produces a sensible impression on a cake of cement prepared in a prescribed manner, the cement shall be considered set.

The last and most important of all the tests to which Portland cement is submitted is that of soundness. It is the one quality which is indispensable. It has been already said that our chemical knowledge is insufficient to enable us to tell by any process of chemical enquiry whether a given sample of cement is sound or not, and once more perfectly empirical methods are resorted to. All depend on observing whether the cement when set remains so nearly constant in volume that the conclusion may safely be drawn that in use it will remain unaltered in form, and that its internal stresses will be too slight to impair its strength in any important degree. Early and crude methods of a purely qualitative kind need not detain us, and we need only consider tests which give a *measurement* of any alteration of volume. Of these, two are generally regarded as both simple and adequate. Direct measurement of a bar of known length by micrometer calipers as in the Bauschinger apparatus is as satisfactory a method as could well be conceived, and but for the need of an appliance so simple and cheap as to be fit for workshop use it would probably now be standard. It is just this simplicity and cheapness which has caused preference to be shown for the Le Chatelier apparatus which provides a means, though not a direct one, for measuring the dilatation of the test piece. For its description and mode of use the British Standard Specification may be referred to. (Appendix D., p. 59.)

Tests of this kind will detect with certainty cement which expands seriously after setting, but as in some cases this expansion does not take place at once, but after a period of many weeks, it is perilous to rely on indications obtained in a

comparatively few days. Hence the tests are usually accelerated by keeping the test pieces at a higher temperature than that of the air so as to hasten the reactions occurring within them—the most commonplace laboratory device for expedition. It may sometimes happen that a cement of dubious integrity which would have pulled through a cold test conveniently delayed for the adjustment of its internal stresses, breaks down when subjected to an accelerated test, but that is a small matter compared with the safety secured by the more rigorous method. That no practical difficulty exists in meeting the requirements of a properly devised accelerated test is proved by the fact that not only has that test been incorporated in our standard specification, but the permitted limit of expansion has been decreased since its adoption.

It is right to say that this test is vigorously opposed in some countries, but it is fair to our own people to add that British makers have accepted it and successfully met its demands ; it would be “rubbing it in” to comment on such a situation.

It would be a delightful exercise to provide additional criteria for the determination of cement, and such an exercise may be commended to the ingenious ; but in plain practice a specification on the lines of the British Standard Specification is sufficient. Improvement will certainly be made in the direction of stiffening the demands of the consumer, and as these will follow in the ordinary course of trade they need not concern us now. Much more important is the alteration of the specification in principle, which will occur when a method has been devised for determining the proximate composition of cement and for ascertaining the setting time of concrete. At present there is no means of doing either. And as an example of our ignorance of the first, let me say that in spite of the many efforts, some of them intelligent, which have been made to devise a process for the determination of what

is termed "free lime" in cement, not one that has been put forward is reliable; most such attempts are intrinsically absurd. From the nature of the case this could be predicted. There is no difference in essence between "free lime" and lime combined with so feeble an acid as ferric oxide as to be competent to behave towards all reagents in substantially the same way as does free lime, whence it follows that as the latter is necessary and inevitable in cement, the former may be acceptable. All that needs to be ascertained is whether the lime, free or loosely combined, is harmful or not, and here the chemist has recourse to physical methods so simple that he must marvel at his own thick-headedness in devising anything less obvious. By the measurement of the volume occupied by a given quantity of set cement under conditions at least as severe as those occurring in practice, and ascertaining that that volume is invariable (except by ordinary dilatation and contraction due to heat and cold) the stability of that cement will be decided upon with accuracy, and irrespective of its composition. The determination of "free lime" becomes a question rather worse than academic.

Originally the sole object and use of cement of the Portland class was to replace common lime in situations where exposure to water by frequent wetting or actual immersion made the latter material unreliable or useless. In former years the high cost of Portland cement, 4*os. od.* and more a ton, as against 1*os. od.* to 2*os. od.* for lime, seemed to forbid the employment of the former when lime would do. In addition, lime-mortar is a far easier material to be prepared and used than is Portland cement mortar, and there is less risk of its being spoiled by careless and dilatory handling. Besides this, up to some twenty years ago there was some uncertainty whether Portland cement could be regarded as a perfectly dependable material. If it *had* to be used, as in under-water work, used it was; but failures were not unknown, the causes of which at that date were often

obscure, leading to a lack of confidence in cement as a general structural material. The combined effect of these influences was to limit the use of cement to those purposes for which it was practically indispensable. When, however, by improved methods of manufacture, notably by the introduction of the rotatory process, the price of cement came down to something like £1 a ton, while the price of lime suffered no corresponding decline, and the quality of the product improved in a similar degree, the question assumed a different aspect, and at the present time Portland cement is used as a matter of course in every kind of structure irrespective of whether it is exposed to water or not. Its great mechanical strength is in itself an advantage when solidity is all-important, and remains an advantage when a structure of ordinary solidity is to be made cheaply by freely diluting the cementitious substance with local and cheap aggregate. When to this is added the merit that cement suitably diluted has a coefficient of expansion almost identical with that of steel, that the adhesion of cement to steel is excellent, and that the corrodible metal is admirably protected by its envelope of cement, the success of composite structures of cement and steel connoted by the term ferro-concrete is as large as would be predicted on general principles. In fact, up to the present time and with our present knowledge there appears to be no limit to its application as the principal structural material for buildings which, while not extravagant in cost, shall be permanent within the life of a nation—a matter at the most of a couple of thousand years.

The unintelligent application of cement leads easily to errors which may be disastrous. It is not enough that the engineer armed with full knowledge of the strength of his material shall so design his structure that it shall resist all probable mechanical stresses. He must be advised by the chemist concerning its resistance to attack by influences far more subtle, deadly, and powerful than mechanical forces.

Their slow operation forbids reliance on any direct test such as the loading of a bridge with dead weight or a live load, and recourse must be had to a knowledge of the causes which allow a material to remain in a state of chemical equilibrium almost indefinitely or indicate that the equilibrium is so mildly stable—so meta-stable—that its destruction is easily within the purview of the chemical seer.

To come to particulars in this matter. The cement itself must be so well made that when set it shall be free from internal causes of decay. On account of the fact that the process of setting takes a time which varies from a few minutes to a few hours, the user must occur within those limits. Because setting is much influenced by such external influences as temperature and moisture, both must be regarded in applying the material. Obviously it is futile to put a slow-setting cement into a position where it will be washed away before it has had time to set; equally absurd would it be to make a quick-setting cement into a mortar and utilise this after a Long Vacation. Such evident mistakes are a mild example of what disasters may attend unintelligent use of cement. There are many others less easily foreseen and on that account involving worse results. It must be remembered that all the products of the setting of cement are attackable by water. Hence although capable of setting under water and remaining immersed in water without destruction, cement will be destroyed when it is subjected to the action of water continually renewed. If the products of the reaction are carried away rapidly, the rate of destruction necessarily increases, and thus it comes about that water flowing through concrete is fatal to that concrete's stability. On this account it is one of the chief objects of the engineer responsible for structures which are exposed to running water or to the constantly moving water in a tideway to ensure that his structure is impervious, whatever the character of the water

may be. So completely true is this dictum that if the water were distilled he would be not less but more concerned to make the structure impervious. For this end the usual and sufficient practice is to avoid skimping the cement, but there are other methods at least as necessary and not so often adopted. It is not so common to prepare a concrete which shall be free from voids—a matter to be touched on later—and it is still less common to provide a material capable of combining with the hydrated lime set free in the process of the setting of the cement and forming with it a true cement, itself impervious. Substances having this property are of course of the pozzolanic class, and are often locally available. Anything like trass or well-burnt clay or good granulated blast furnace slag intimately ground together with cement in quantity sufficient to combine with that proportion of the lime which in the setting of cement *per se* is set free and is open to easy attack by water, will not only make the concrete of which it forms part far less pervious, but will increase its mechanical strength substantially. The only objection to this procedure is the difficulty of ensuring a thorough combination of the pozzolanic material on the work, but there is no reason why the cement maker should not either grind the pozzolana finely and sell it as such or prepare a mixture of cement and pozzolana in proper proportions and sell that under some trade name distinguishing it from unmixed cement. It has been urged against this method that if admixture of any kind were allowed, a door would be open to fraud, but it appears to me that the situation would be unchanged. Most small users of cement buy that material confiding in the honesty of the maker, and they would continue to accept his guarantee that the substance sold was Portland cement and pozzolana. Large users are well able to protect themselves. Taking into account the great advantage arising from the use of a

pozzolana both in respect of the increase of strength of the concrete, its greater imperviousness, and its resistance to the dissolving action of water, the possible slightly greater chance of fraudulent admixture may be regarded as without practical significance.

What has been said concerning the necessity for ensuring that concrete shall be as dense as possible applies with even greater force to the case of reinforced concrete where the integrity of the structure depends upon the protection of its metal reinforcements from corrosion. It may be accepted that the alkaline environment provided by the cement will inhibit the rusting of the iron provided the two materials are in good contact with each other, but if by chance there are gaps or cavities so that the metal is not thus protected, rusting may occur from incursion of water, especially if that be saline. It is therefore highly desirable that the concrete should be impervious, and, in consequence, the steel protected not merely by the accidental alkalinity of its surroundings by being hermetically enclosed.

The aggregate used in the preparation of concrete will vary in size from huge blocks or displacers weighing tons down to the finest sand. It must be so proportioned that the finished concrete is almost free from voids, that is, shall have a specific gravity nearly equal to the mean specific gravity of its components. If the average specific gravity of a siliceous aggregate such as Thames ballast is taken as 2·6 and that of set cement as the same, the mean specific gravity of any mixture will be, of course, 2·6, corresponding with a weight of 162·5 lbs. per cubic foot. It is rare to find so high a figure in practice—140 lbs. is nearer the mark, whence it follows that almost 14 per cent. of the apparently solid concrete consists of voids—roughly one-seventh of its total bulk. There is no doubt that scarcely any pains are too great to ensure the closeness of texture of concrete destined for work of

importance, for in difficult situations and especially where flow of water or intermittent exposure to water as in a tideway has to be faced, the stability and permanence of the structure is very largely controlled by this all-important quality of imperviousness.

With regard to the *nature* of the aggregate a little may usefully be said. Any material which is hard, preferably sharp and having a surface not quite smooth and chemically stable, may be used, choice naturally falling on the substances available on the spot where the concrete is to be made. It is only rarely that a doubt arises whether a given material may be safely used, and then the doubt can usually be resolved on chemical grounds. Débris containing sulphates, and slags consisting of easily decomposable silicates or oxidisable constituents would be condemned, and potential sulphates in the shape of pyrites might lead to the rejection of a rock otherwise perfectly suitable.

It is not from such causes that failure of cement concrete commonly occurs. Generally destruction is wrought by attack from without, not by treachery within, and is brought about by substances capable of attacking the very basic compounds of which cement consists. Evidently all acids, even carbonic acid, which form soluble lime salts, are to be feared, and in addition neutral salts of metals whose oxides are less basic than lime. Sulphates of such metal are especially obnoxious, as not only are the lime compounds constituting the cement broken up, but the product, calcium sulphate, in its turn acts upon the aluminares of the cement with surprising vigour. I have seen important structures seriously impaired and even imperilled by such an action.

As sea water contains magnesium salts in abundance and an appreciable amount of calcium sulphate, its destructive action on cement is considerable, and only by careful exclusion either by such means as stone-facing or by making the

concrete so dense that inflow and outflow of the water into its substance cannot take place, and attack must proceed entirely from without, are stability and permanence possible. The product of reaction of magnesium salts on the lime compounds in cement is, of course, magnesium hydroxide, and in earlier days ludicrous mistakes arose from this fact. Deposits consisting substantially of hydrated magnesia were found in cement structures which were perishing in the sea, and examined by chemists whose precision of analysis was adequate, but whose purview remained within their laboratory. The presence of "magnesia in the cement" was announced, and the engineer whose purview lay wholly outside interpreted this as meaning that the magnesia had its origin in the cement and sought to exclude it from the commodity he bought. As it happened that about the same date failure had occurred in various structures made with cement, which truly contained unusually large proportions of magnesia, a fine confusion of thought arose, and it is only lately that the magnesia question has properly settled down into deciding what is the largest percentage of magnesia that can be present in Portland cement without risk of failure. Authorities differ, and to be on the safe side the British Standard Specification has fixed 3 per cent. In other countries where magnesian materials are common this limit may well be extended, but far greater knowledge acquired either by a study of the true chemistry of cement as distinct from its ultimate composition, or by the observation of the behaviour of cements of known origin and composition under known conditions for considerable periods of time, will be necessary before a standard which, while including all useful cements whatever their content of magnesia, will rule out all those likely to be dangerous, can be set even tentatively.

Apart from such chemical causes it goes without saying that such mechanical agencies as frost and erosion by water or

air carrying suspended matter are operative against cement as they are against masonry or brick, but as the degree of their destructive activity is independent of the fact that the material attacked is *cement*, their discussion would be best undertaken in an essay on the stability in *these* respects of structural materials at large, and should not be included in the present narrower theme.

In the previous lecture some indication was given of the kind of work which must be undertaken by the technical adviser, whether consultative or resident, of a cement undertaking to be started or in operation. The kind of training which he should undergo may now be considered, and conjoined with that the sort of knowledge which that training will bestow on him.

Assuming that he has been decently educated in an elementary sense—and by that I include the rudiments of literary as well as scientific knowledge—it is essential that he shall have a thorough and rigorous training as a chemist, and to this end, for all but the highly exceptional man who is beyond rule, it is of primary importance that he shall be given all the advantages of fuller and continued education in an institution with adequate resources certainly, but, better than that, informed and inspired with a spirit at once serious and liberal such as that of the college in which we are gathered. I will leave to those who by special study of the subject, or by the admirably exacting school of practical teaching, have made themselves educationists in the true sense of the word, the pleasant duty of laying down the best course of preliminary study for the chemist who is to concern himself with the cement industry, merely entering a strong plea that the course should be as wide as the time available permits, that some mechanical training should be included, and that all specialisation should be postgraduate. In attaining this end the Institute of Chemistry has a dominating influence as it

insists, and rightly insists, that candidates shall show a sound general knowledge of chemistry as a science before they can be hall-marked as competent and equipped with professional knowledge, and this irrespective of their narrower special knowledge, however profound that may be.

The second or postgraduate training of a cement chemist may take place in a college within easy hail of some centre of the cement industry, or in the laboratory of some practitioner similarly placed. It is of high importance that the learner should have access to a works and realise that laboratory operations when translated into manufacturing processes assume a novel and often startling appearance; that the little niceties of the laboratory are often worse than useless in a works, and *per contra* that difficulties which do not occur or are insignificant under laboratory conditions may turn the scale between manufacturing efficiency and failure, between profit and loss. He must learn to think in tons instead of grammes, in steel and firebrick instead of platinum and porcelain. A native sense of proportion and steady remembrance of the fact that it is impracticable to alter the scale of any operation in the ratio of even 1 to 1,000 and to maintain identity of operation will soon teach him to put aside the details of his laboratory knowledge and to hold fast by the principles on which that rests.

From the time, some twenty-five years since, when I first began to concern myself with cement, its chemistry, though not precisely in a state of flux, has remained in the condition proper to good clinker when in the sintering zone; it has been sticky and plastic. There are signs, however, that this era is coming to an end, and I look forward to reading in my old age and retirement controversies briskly carried on concerning the rôle played by, say, Digammalite (consisting of a solid solution of hepta-calcium titanate and endekka-barium ferrite) in

influencing the coefficient of dilatation of blast furnace cement—Portland cement being then obsolete.

Pending this degree of precision one must take what one can get.

It is common knowledge that Portland cement consists substantially of lime united in some way with silica and alumina, both acting as acid oxides. Such ingredients as are present in substantial amount, for example, ferric oxide and magnesia, no doubt play a part; but as true Portland cement can be made with materials from which they are absent, discussion of the chemistry of cement is simplified by ignoring them.

Le Chatelier, who is the father of the modern chemistry of cement, believed that the essential constituents are tricalcium silicate (3CaO SiO_2) and probably tricalcium aluminate ($3\text{CaO Al}_2\text{O}_5$), and prepared the latter by direct fusion of its components, but failed to obtain the former by the same means. However, using the artifice of providing a flux, calcium chloride, to induce the union of the lime and silica, he obtained the compound SiO_2 , 2CaO , CaCl_2 , in which the calcium is already in the correct ratio to the silicon, and on decomposing this with steam at a temperature above the dissociation temperature of $\text{Ca}(\text{OH})_2$ obtained tricalcium silicate, not quite pure, as calcium chloride remained to the extent of 1·2 per cent. of the mass.

Later experimenters have confirmed the existence of tricalcium aluminate as an essential constituent of cement, but were inclined to doubt the existence of tricalcium silicate, holding that the body synthetically prepared by heating lime and silica together in the proportion indicated by the formula, in reality consists of an intimate mixture of lime and calcium orthosilicate 2CaO SiO_2 . Within the present year, however, the claim of tricalcium silicate to individual existence has been rehabilitated, it being now maintained that the former

observations showing that a mixture in that proportion contains only CaO and 2CaO SiO_2 were in themselves exact, but that the conclusion drawn from them is invalid because tricalcium silicate made from pure lime and pure silica is unstable at its melting point; if, however, such a mixture is maintained for some time at a lower temperature, *e.g.*, about $1,800^\circ \text{ C.}$, or if a small quantity of alumina (as little as 0·5 per cent.) be present, true tricalcium silicate is obtained. Accepting this as the best current knowledge, it is interesting to note that just as in the earlier work of Le Chatelier the presence of a *tertium quid*, in his case calcium chloride, in the later instance calcium aluminate, is necessary to ensure the formation and continued existence of this most elusive body.

As it is impracticable to prepare Portland cement having the proportions indicated by the equation

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 3$$

on a manufacturing scale, and to cause the acid and basic oxides there represented to unite perfectly, it is necessary that to ensure the absence of uncombined lime the acid oxides should be somewhat in excess and the ratio given be slightly below 3. It follows that in addition to tricalcium silicate and tricalcium aluminate there will necessarily be present a lower silicate, namely, the orthosilicate 2CaO SiO_2 , and probably a lower aluminate, *e.g.*, $5\text{CaO } 3\text{Al}_2\text{O}_3$ and $\text{CaO Al}_2\text{O}_3$, and in addition such minor constituents as magnesia and oxide of iron free or combined. We know too little of the rate at which union of the chief basic and acid oxides can be induced to take place at a merely sintering temperature to allow us to do more than approach the limit set above, but it is reasonable to conclude that the closer the approximation the better the product. As an example may be given the percentage composition of a cement composed of

tricalcium silicate, tricalcium aluminate and dicalcium silicate in such proportions that an ample supply of alumina is present (5 per cent.) to induce the formation of tricalcium silicate and that the ratio of acid to basic oxides shall not exceed 1 : 2·9 is

	Per cent.		Corresponding with		Per cent.
SiO ₂ ...	23·49	...	3CaO SiO ₂ ...	79·11	
Al ₂ O ₃ ...	5·00	...	3CaO Al ₂ O ₃ ...	13·23	
CaO ...	71·51	...	2CaO SiO ₂ ...	7·66	
	<u>100·00</u>			<u>100·00</u>	

A cement of this composition would terrify the average user; but according to the best knowledge we now possess, it would be perfectly safe and of admirable quality.

In like manner, if a cement be constructed consisting of 20 equivalents of tricalcium silicate, one of tricalcium aluminate and one of dicalcium silicate, it will have the ultimate composition

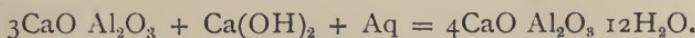
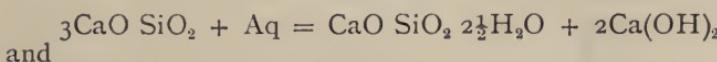
	Per cent.
SiO ₂ ...	25·19
Al ₂ O ₃ ...	2·04
CaO ...	72·77
	<u>100·00</u>

an even more blood-curdling compound, but one which quite possibly could be made, and if made could certainly be safely used.

The composition of cement, other than Portland cement, has received less study; but it is probable that when the constitution of the latter has been further worked out the data can be applied fairly easily to these less important materials. They will come under the general head of lime-silica-alumina compounds, a subject which has already received great and fruitful attention, and will fall into their places as examples of the generalisations thus obtained. Similarly the slag cements consisting of blast furnace slag,

which, by suitable heat treatment sets *per se*, will have the mechanism of its formation explained by the same class of research and as a practical corollary, the somewhat empirical methods now in use for manufacturing these materials will be superseded by a strictly scientific procedure. Success in this direction may have an important influence on the cement industry at large.

The chemical changes accompanying the setting of Portland cement have been the subject of almost as much study and dispute as has the constitution of the cement itself. Two views are now current and worthy of attention. The first is that the cementitious calcium silicates and calcium aluminates are hydrated and caused to crystallise in the same way as that generally accepted to be true of plaster of Paris, that is, the water used in gauging dissolves a portion of these bodies and forms a supersaturated solution which then deposits crystals of the hydrated compounds and renders the water competent to dissolve another portion of the anhydrous substances, again to form a supersaturated solution, and again to deposit crystals. Now that tricalcium silicate has been rehabilitated, no better representation can be given than that shown by the original equations of Le Chatelier—



It will be observed that in the act of setting, two-thirds of the whole of the lime pertaining to the tricalcium silicate is set free, and that even allowing for the combination of a part of this with tricalcium aluminate to form the tetra calcium aluminate (hydrated) there will be a substantial quantity over—as in fact there is.

It must not be assumed that there has been rigorous proof of all stages of this explanation, but it is consonant with

those facts which are known and is based on the careful and conclusive work which has been done on the setting of plaster of Paris.

The second view of the setting of Portland cement is sharply differentiated from the foregoing in that the essentially cementitious product is believed to be a gel, and depends on the observation that when the hydration of finely-powdered cement is watched under the microscope gelatinous products are formed which are regarded as hydrated calcium silicates and aluminates in a colloidal condition. That gels are formed is indicated by their power to absorb dyes and become stained, and it is considered that in process of time they take up lime set free by the gradual hydration of the calcium silicate and become indurated.

It is not an agreeable position to be in when one finds oneself unable to pronounce a definite opinion on two hypotheses so different ; but in this case I am forced to it because the data available on both sides appear to me scanty, sketchy or inconclusive, and my own observations made for some technical purpose and necessarily worse than sketchy as a research, have led me to nothing worthy of your consideration. I incline to the crystalline theory, but then the notion of a kind of glue sticking things together—a cement within a cement—is very attractive. I could cite no better instance than this as an example of a matter of primary interest to a great industry, and still not decided by us chemists.

I think that I have said enough to show that the chemistry of cement, far from being dull or obvious, requires the best powers of the most expert and penetrating worker. Mention has already been made of the training necessary to prepare a chemist as an adviser—resident or not—in this industry, but if he is lucky enough to have the opportunity of investigation without regard to immediate needs, whether technical or monetary, he needs equip himself with the best knowledge of mineral

chemistry in its fullest sense. He must *ex hypothesi* be an analyst whose results are so good that no one would dispute them; he must have such a knowledge of petrology as will enable him to make sections of material more friable than most rocks, and thin enough to allow new and rather nebulous bodies to be identified; he must understand methods of measuring heat changes in a mixture brought slowly to, maintained at, or reduced from a given temperature, and to be able to apply these at temperatures when experimental difficulties increase with each degree. He must be conversant with the latest knowledge current among physical chemists, and be sufficiently critical to take to himself all that is good and based on sound work. If he add to that a delight in his work, and just that tincture of originality which removes him from the ranks of mere disciples, he is possessed of equipment sufficient, but none too great, for his task, and I, for one, envy him.

(At the conclusion of the second lecture, Mr. Blount explained the testing machines and a sampler which were exhibited.)

The older form of testing machine, kindly lent by Messrs. Cubitt, embodies the essential features of the more recent type which is now in use. Both are steelyards so arranged that the briquette to be tested is subjected to tensile stress slowly applied. In the modern machine the rate of application of the stress is automatically controlled. The steel-yard is graduated in lbs. per sq. in. (pp. 66—67).

The sampler, the device of which is chiefly due to Mr. Blount's former assistant, Mr. Knight, consists of an iron drum, which can be exhausted by a Fleuss pump, and a steel pipe having perforations at the end, and sufficiently long and slender to penetrate into the heart of a heap of cement, samples of which can by this means be drawn from any depth and received in the drum. Another form of sampler is a tube, containing an Archimedean screw, which in many cases is to be preferred on account of its greater simplicity and because it is free from the defect of the vacuum sampler, which is liable to choke and sometimes to allow fine dust to pass into the pump to the destruction of the latter (p. 65).

APPENDIX A.
ANALYSES OF PORTLAND CEMENT.

ANALYSES OF CEMENT RAW MATERIALS.

49

	Chalk.	Limestone.	Marl.	Clay.	Shale.	Cement Rock.
Moisture	19.03	—	—	—	—	—
Sand	0.93	0.20	15.10	28.42	60.22	24.29
Combined Silica	0.43	—	30.32			
Alumina (Al_2O_3)	0.48	0.08	7.30	15.49	18.10	4.54
Ferric Oxide (Fe_2O_3)	—			7.74	9.10	
Lime (CaO)	42.90	56.02	42.16	2.04	trace	20.76
Magnesia (MgO)	0.42	0.24	0.34	1.96	1.62	12.50
Sulphuric Anhydride (SO_3)	—	—	—	1.96	—	—
Carbonic Anhydride (CO_2)	34.16	43.38	33.51	—	—	37.91
Water, Alkalies and loss	1.65	0.18	1.59	12.07	10.96	
	100.00	100.00	100.00	100.00	100.00	100.00

APPENDIX B.

**METHOD OF ANALYSING PORTLAND CEMENT
AND CEMENT RAW MATERIALS.**

THE analysis is conducted in the following manner :—

(i) *For Silica and Chief Bases.*—0·5 grm. is placed in a shallow dish about 6 ins. in diameter, swirled round with a few c.c. of water until thoroughly mixed. About 20 c.c. of hydrochloric acid of sp. gr. 1·15 are then added, and the swirling continued for a few minutes. The cement is thus dissolved almost completely, and no silica is precipitated. The dish with its contents is placed on a hot plate, taken to dryness, covered with a clock glass, and baked on a triangle at a temperature of at least 200° C. for an hour. This part of the procedure is essential. Silica can be completely dehydrated and rendered insoluble when it is spread out in a thin even film and heated in this manner.

The residue obtained on evaporation in the manner described is digested with about 30 c.c. of hydrochloric acid of sp. gr. 1·15, and the silica, together with the insoluble residue, is filtered off. The filtrate is returned to the dish in which the cement was dissolved, and an excess of ammonia is added. The solution in the dish is gently heated until nearly all the excess of ammonia has been driven off. This stage is one of some delicacy. The removal of the excess of ammonia is necessary to ensure the precipitation of the whole of the alumina ; also the evaporation must not be pushed too far, else some alumina will redissolve. No guide is so

reliable as a well-trained nose. When properly conducted the separation is exact! the whole of the alumina and ferric oxide is precipitated, and the precipitate is free from lime.

The filtrate from the alumina and ferric oxide is collected into a beaker, and to it about 25 c.c. of ammonia (containing half its volume of solution of 0·880 sp. gr.) is added. The mixture is brought to its boiling point, and 25 c.c. of a 4 per cent. solution of ammonium oxalate is poured in. The precipitated calcium oxalate is boiled for two or three minutes, allowed to settle for about an hour, and then filtered. The operation, if properly conducted, will separate all but a very trifling proportion of the lime, and the precipitate will be free from magnesia. The possible remnant of lime is recovered at the next operation.

The filtrate from the calcium oxalate is evaporated in a porcelain dish until a pasty residue is obtained, 40—50 c.c. of nitric acid (sp. gr. 1·4) is added, the dish covered, and the heating continued until the ammonium salts have been broken up and their products volatilised.

The residue, after the destruction of ammonium salts, is dissolved in a few c.c. of water and about six drops of hydrochloric acid of sp. gr. 1·15. Excess of ammonia and two drops of ammonium oxalate solution (4 per cent.) are added, and the mixture is heated. A small precipitate is obtained, which is filtered off. In ordinary routine work it usually weighs about 0·0015 grm., and consists of about 0·0010 grm. of silica, and the balance of alumina, ferric oxide, and lime. The two latter belong to the cement, and in specially close work must be separated and added to the values for the main precipitates. Under ordinary conditions this is scarcely necessary. The silica is most probably derived from the glass and porcelain vessels which have been used, and partly, perhaps, from the dust inevitable in a city atmosphere. It is better neglected. The filtrate from this small precipitate

contains the whole of the magnesia in concentrated solution, free from excess of ammonium salts and easy to precipitate cleanly and completely. To obtain it, 10 c.c. of ammonia (50 per cent. of 0·880 solution) and 2 c.c. of a 10 per cent. solution of sodium phosphate are added. On shaking and standing for two hours a well-crystallised precipitate is obtained, which is filtered and washed with ammonia (25 per cent. of 0·880 solution). The various precipitates are dealt with as follows:—

The silica and insoluble residue, the alumina and ferric oxide, and the lime as calcium oxalate, are dried and placed, together with their filter-papers, in platinum crucibles and burnt off gently at the mouth of a gas muffle; when the paper is consumed and the calcium oxalate is decomposed to carbonate or thereabouts, the three crucibles are placed inside the muffle and ignited at the full temperature attainable (about 1,050° C.) for one hour. Two sets of precipitates are commonly worked off in a single muffle.

By this means all are brought to the state of anhydrous oxides and, except in rare cases, need no re-ignition. The magnesium ammonium phosphate is burnt off moist in its filter-paper in porcelain at the mouth of the muffle, brushed out, and weighed as pyrophosphate.

(2) *For Insoluble Residue and Sulphuric Anhydride.*—A second portion of 0·5 grm. of cement is decomposed as before, and evaporated to dryness in the same way. As it is not intended for the determination of silica, there is no need to bake the residue. The contents of the dish are taken up in 10—15 c.c. of hydrochloric acid of sp. gr. 1·15 and filtered, leaving as much as possible of the residue in the dish. The silica on the filter is washed back into the dish and digested with a saturated solution of sodium carbonate (not caustic soda). The whole of the silica active and useful in the cement is dissolved, and the inert acid silicates are left.

This insoluble residue is most thoroughly washed, ignited

at the mouth of a gas muffle, and weighed, and the weight is deducted from that of the silica *plus* insoluble residue obtained from the previous portion, thus giving the quantity of combined effective silica.

The original acid solution from this second portion of 0·5 grm. is precipitated with 5 c.c. of a saturated solution of barium chloride at the boiling temperature. The boiling is continued for about three minutes, and after standing for one to two hours, the solution is filtered and the barium sulphate, moist, together with the filter-paper, is ignited at the mouth of a gas muffle and weighed.

(3) *For Loss on Ignition; Carbonic Anhydride and Water.*—0·5 grm. of the cement is ignited in platinum for half an hour in a gas muffle at a temperature well below the maximum obtainable, e.g., about 800° C.

(4) *For CO₂.*—2 to 5 grms., according to the character of the cement, are decomposed with hydrochloric acid in the ordinary manner, and the CO₂, after purification through a silver sulphate tube and drying, as usual, is collected in a weighed potash bulb.

(5) *For Alkalies.*—1 grm. of the cement is decomposed in the way already described, and the silica and chief bases got out as usual. The ammonium salts are destroyed with nitric acid, and the final residue, containing magnesia and alkalies, is treated with baryta and afterwards with ammonium carbonate, and the alkalies are converted into chlorides, weighed as such, and separated by the use of platinum chloride.

(6) *Separation of Alumina and Ferric Oxide.*—This may be carried out on the mixed precipitate after ignition, or on a separate portion of cement. In the former case the precipitate is fused with potassium bisulphate and the melt dissolved in hydrochloric acid. The solution is precipitated with ammonia, dissolved in hydrochloric acid, the solution concentrated, and poured into excess of caustic soda prepared from

the metal. The alkaline solution is heated to near boiling, to ensure the dissolution of the alumina. The operation is best conducted in platinum. The solution is diluted so as to allow it to be filtered through paper, and the ferric oxide collected, dissolved in hydrochloric acid, and precipitated with ammonia, filtered, ignited, and weighed. The ignition may be performed over a Bunsen burner, as there is not the same difficulty in completely dehydrating ferric oxide as there is with alumina. If desired, and as a check, the alumina is recovered from the caustic soda solution.

It is generally more convenient to obtain the joint ammonia precipitate from another portion of the cement, and to separate the ferric oxide and alumina in this by the caustic soda process; the bisulphate fusion and recovery of the oxides from the melt are thus avoided. In the event of manganese being present in sensible amount, as it is in Roman and Medina cements, and in cements made from blast furnace slag or adulterated with the same material, the ammonia precipitation must be carried out in the presence of bromine. Using a little bromine throughout, the manganese finally appears with the iron, and can be satisfactorily separated by a basic acetate precipitation.

A more rapid determination of iron, sufficiently accurate for all practical purposes, may be made as follows:—1 grm. of cement is treated with water and dissolved by the addition of a few c.c.s of hydrochloric acid in a small conical flask. After solution, 3—4 grms. pure granulated zinc (free from iron) are added and the flask closed with a cork fitted with a Bunsen valve. When all the iron has been reduced to the ferrous state, and the zinc dissolved, the cooled solution is poured into 200—300 c.c.s air-free distilled water, excess of sulphuric acid added, and titrated with $\frac{N}{20}$ KMnO₄ solution. Since the reagents used are never absolutely free from iron, it

is advisable to make a blank determination under exactly the same conditions prevailing in the actual estimation.

(7) *For Sulphides*.—In general, these are present in such small quantity that they may be ignored. They are, however, of more importance when slag products are treated. The best process is to dissolve the cement in hydrochloric acid in an atmosphere of coal-gas, and collect the H_2S in lead acetate solution, finally weighing the precipitated sulphide as lead sulphate.

ANALYSIS OF RAW MATERIALS.

Limestones, if nearly pure, may be analysed as described under cement. It is not usually necessary to treat the insoluble siliceous matter with Na_2CO_3 , but, after ignition, it should be treated with HF and H_2SO_4 and ignited. The residue, if appreciable, is fused with Na_2CO_3 and analysed in the usual manner.

For siliceous and argillaceous limestones which contain a considerable amount of insoluble matter it is advisable to adopt the following procedure:—1 grm. of the finely ground sample is ignited in a platinum crucible at the full temperature of the muffle for about an hour. In this way the whole of the constituents are rendered soluble (unless the limestone is so siliceous that the lime present is insufficient to flux the whole of the siliceous matter), and the residue, after weighing (to determine loss of weight on ignition), may be analyzed exactly as described under cement. In all cases the purity of the silica should be tested by means of HF and H_2SO_4 .

In the case of dolomitic limestones it is advisable to redissolve the ferric oxide and alumina, and lime precipitates, and to reprecipitate them in order to ensure their freedom from magnesia.

Separate portions are taken for the determination of SO_3 and CO_2 in the usual manner.

Occasionally limestones are met with containing appreciable quantities of pyrites. This constituent is best determined by boiling 1—5 grms. of the finely powdered sample with aqua regia, removing nitric acid by evaporation with excess of hydrochloric acid, and precipitating the total SO_3 in the diluted filtered solution by means of barium chloride. In calculating the amount of pyrites present, allowance must be made, of course, for sulphur existing as sulphuric anhydride in the limestone.

Clay, Shale, &c.—0·5 grm. of the sample, finely ground in an agate mortar, is thoroughly mixed with 2·5—3 grms. pure Na_2CO_3 in a platinum crucible and heated in a muffle furnace to a temperature just sufficient to fuse the mixture, with occasional shaking, for about half an hour. (In some cases a more liberal allowance of Na_2CO_3 may be necessary.) When cold the fused mass is transferred to a shallow platinum or porcelain basin, digested with hot water, and, after disintegration, dissolved by the addition of hydrochloric acid. The solution is evaporated to dryness and baked for the estimation of silica as described under cement. The filtrate from the silica should be evaporated and baked a second time in order to separate a further small quantity of silica which usually remains soluble after one baking only. From this point the analysis is conducted exactly as described under cement, care being taken to wash the various precipitates free from alkali, bearing in mind also the necessity for double precipitation should a large proportion of magnesia be present. The purity of the silica is, of course, tested by means of HF and H_2SO_4 .

The alumina and ferric oxide are separated by fusion with potassium bisulphate as described in the analysis of cement. For rapid work the bisulphate melt may be dissolved in dilute hydrochloric acid, reduced with zinc and titrated with permanganate solution.

The estimations of "loss on ignition," SO₃ and CO₂ are made in the usual manner.

The estimation of pyrites is sometimes necessary, and may be made as described under the analysis of limestones.

It is not usually essential to estimate alkalies in cement raw materials, but should it be required to complete an analysis, 1 grm. of the finely ground sample is decomposed by evaporation with HF and H₂SO₄. After removing the excess of sulphuric acid at a gentle heat, the residue is dissolved in hydrochloric acid, the chief bases removed as usual, and the determination completed as described in the analysis of cement.

For shales and clays which contain a considerable quantity of calcareous matter it is advisable to extract the sample with hydrochloric acid and to analyse the soluble and insoluble portions separately, the former as described under cement, and the latter by fusion with sodium carbonate as described under clay.

APPENDIX C.

METHOD OF PREPARING CEMENT FROM RAW MATERIALS ON AN EXPERIMENTAL SCALE.

Preparation of Slurry.—About 5 kilos of raw materials, crushed to pass a 7×7 sieve, are mixed in the required proportions and introduced into a ball mill. Sufficient water is added to produce an easily workable slip. When the material is sufficiently ground (*i.e.*, when an even slime is produced in which no gritty particles can be felt, the whole passing 180×180 -mesh sieve), the slurry thus obtained is run out and dried to a plastic state. This is then cut up into convenient form, *e.g.*, sticks of $\frac{1}{2}$ -inch cross-section, and thoroughly dried.

Furnace.—The furnace used is shown in the accompanying diagram and consists of firebricks placed so as to form a box which is lined with Portland cement. At the back of the furnace a gas-injector is fitted. The front and top of the furnace are removable to allow for charging and drawing.

Burning.—A charge of dried slurry is introduced into the furnace and the temperature raised to such a point as is required to clinker the material. After 15 to 20 minutes the charge is withdrawn and a fresh charge of slurry introduced. When the whole of the slurry has been burnt in this way it is allowed to cool and is finally ground in a ball mill.

APPENDIX D.

SIGNIFICANT CLAUSES OF THE BRITISH STANDARD SPECIFICATION FOR PORTLAND CEMENT.

(Abstracted by permission of the Engineering Standards Committee from Report No. 12. Revised August, 1910.)

Composition and Preparation of Cement.—The cement shall be prepared by intimately mixing together calcareous and argillaceous materials, burning them at a clinkering temperature and grinding the resulting clinker, so as to produce a cement capable of complying with this specification.

Tests.—The sample or samples shall be tested in the manner hereinafter mentioned for :—

- (a) Fineness,
- (b) Specific gravity,
- (c) Chemical composition,
- (d) Tensile strength (neat cement),
- (e) Tensile strength (cement and sand),
- (f) Setting time,
- (g) Soundness,

and before any sample is submitted to tests (d), (e), (f) and (g), it shall be spread out for a depth of 3 inches for 24 hours in a temperature of from 58 to 64 degrees Fahrenheit.

(a) *Test for Fineness.*—The cement shall comply with the following conditions of fineness. 100 grammes (4 oz. approximately), of cement shall be continuously sifted for a period of 15 minutes on each of the undermentioned sieves

and in the order of succession given below with the following results :—

- (1) The residue on a sieve $180 \times 180 = 32,400$ meshes per square inch, shall not exceed 18 per cent.
- (2) The residue on a sieve $76 \times 76 = 5,776$ meshes per square inch, shall not exceed 3 per cent.

(b) *Test for Specific Gravity.*—The specific gravity of the cement when fresh burnt and ground shall be not less than 3.15, or 3.10 provided that the Vendor satisfies the Purchaser that the cement has been ground for not less than four weeks.

(c) *Test for Chemical Composition.*—The cement shall comply with the following conditions as to its chemical composition. The proportion of lime to silica and alumina shall be not greater than the maximum nor less than the minimum ratio (calculated in chemical equivalents), represented by

$$\frac{\text{CaO}}{\text{SiO}_2 + \text{Al}_2\text{O}_3} = 2.85 \text{ or } 2.0 \text{ respectively.}$$

The percentage of insoluble residue shall not exceed 1.5 per cent.; that of magnesia shall not exceed 3 per cent.; and the total sulphur content calculated as sulphuric anhydride (SO_3) shall not exceed 2.75 per cent. The total loss on ignition shall not exceed 2 per cent. unless it can be shown that the cement has been ground for more than four weeks.

(d) *Test for Tensile Strength (Neat Cement).*—The average breaking stress of the briquettes 7 days after gauging must be not less than 400 lbs. per square inch of section.

The average breaking stress of the briquettes 28 days after gauging must show an increase on the breaking stress at 7 days after gauging of not less than :—

25%	when the 7-day test is above 400 lbs. and not above 450 lbs.
20%	" " "
15%	" " "
10%	" " "
5%	" " "

450 lbs. " 500 lbs.
500 lbs. " 550 lbs.
550 lbs. " 600 lbs.
600 lbs.

(e) *Test for Tensile Strength (Cement and Sand).*—The cement shall be tested by submitting to a tensile stress briquettes prepared from one part by weight of cement to three parts by weight of dry standard sand, the said briquettes being of the shape described for the neat cement tests.

The average breaking stress of the cement and sand briquettes 7 days after gauging must be not less than 150 lbs. per square inch of section.

The average breaking stress of the briquettes 28 days after gauging must be not less than 250 lbs. per square inch of section, and the increase in the breaking stress from 7 to 28 days must be not less than :—

25%	when the 7-day test is above 200 lbs. and not above 250 lbs.
15%	" " " 250 lbs. " 300 lbs.
10%	" " " 300 lbs. " 350 lbs.
5%	" " " 350 lbs.

(f) *Test for Setting Time.*—Unless a specially slow setting cement is required of which the minimum time of setting has been specified, the cement shall be of one of three distinct gradations of time of setting, designated as “Quick,” “Medium,” and “Slow.”

Quick.—Initial setting time not less than two minutes.

Final setting time not less than ten minutes, nor more than thirty minutes.

Medium.—Initial setting time not less than ten minutes.

Final setting time not less than half an hour, nor more than two hours.

Slow.—Initial setting time not less than twenty minutes.

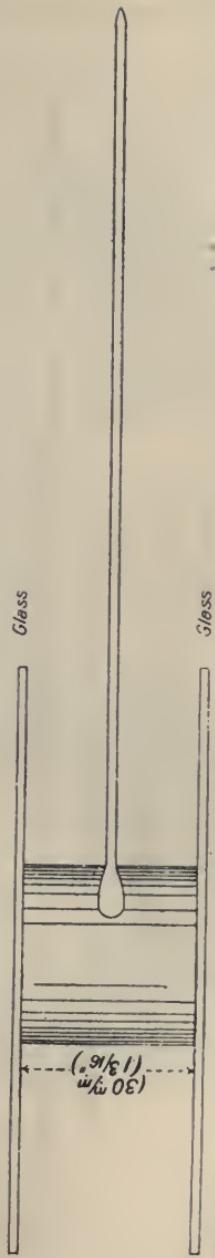
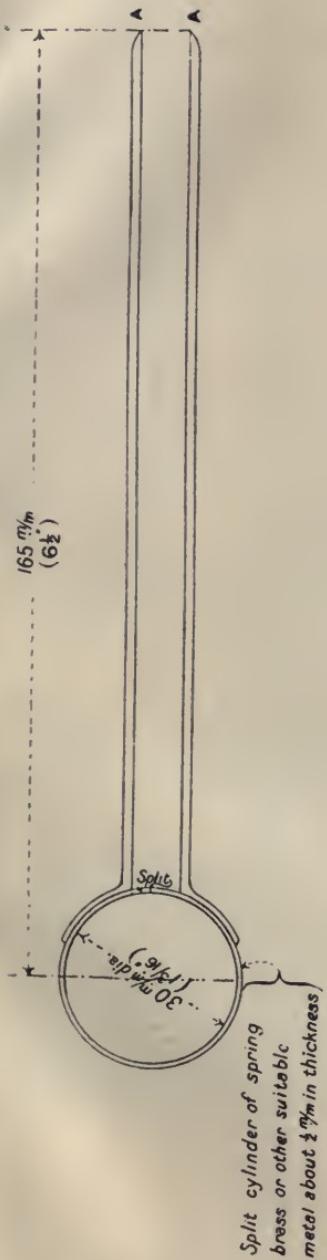
Final setting time not less than two hours, nor more than seven hours.

(g) *Test for Soundness.*—The cement shall be tested by the Le Chatelier method. The apparatus for conducting the Le Chatelier test (Fig. D.) is to consist of a small

split cylinder of spring brass or other suitable metal of 0·5 millimetre (0·0197 inch) in thickness, forming a mould 30 millimetres ($1\frac{3}{16}$ inches) internal diameter and 30 millimetres high. On either side of the split are attached two indicators with pointed ends AA the distance from these ends to the centre of the cylinder being 165 millimetres (6 $\frac{1}{2}$ inches).

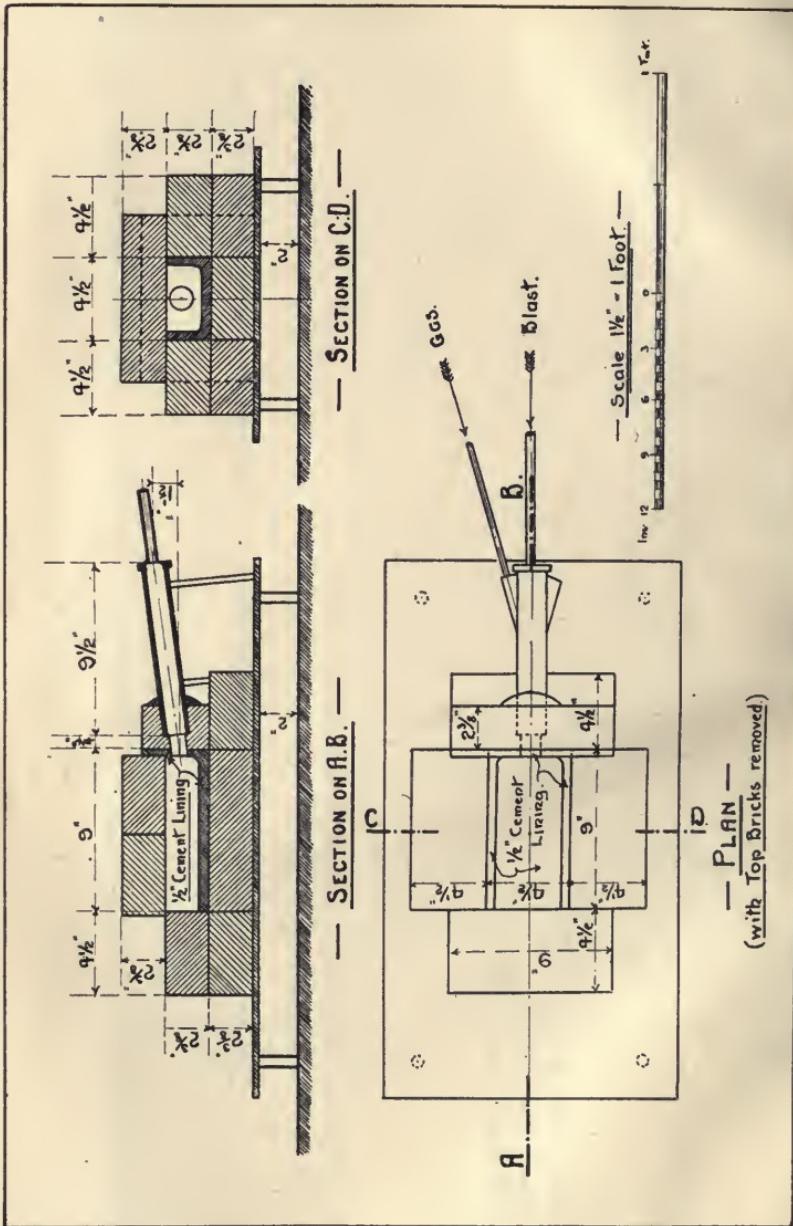
In conducting the test, the mould is to be placed upon a small piece of glass and filled with cement gauged in the mode and under the conditions referred to in Section (d) of Clause 7, care being taken to keep the edges of the mould gently together whilst this operation is being performed. The mould is then to be covered with another glass plate, a small weight is to be placed on this and the mould is then to be immediately placed in water at a temperature of 58 to 64 degrees Fahrenheit, and left there for twenty-four hours.

The distance separating the indicator points is then to be measured, and the mould again placed in water at 58 to 64 degrees Fahrenheit, which is to be brought to boiling point in 25 to 30 minutes and kept boiling for 6 hours. After removing the mould from the water and allowing it to cool, the distance between the points is again to be measured ; the difference between the two measurements represents the expansion of the cement, which must not exceed the following limits, viz.:—10 millimetres when the sample has been aerated for 24 hours in the manner hereinbefore described ; or, if the above test has failed, 5 millimetres after the sample has been aerated for 7 days in the same manner.



ENGINEERING STANDARDS COMMITTEE APPARATUS FOR CONDUCTING THE "LE CHATELIER" TEST.

FIG. D.



EXPERIMENTAL FURNACE FOR MAKING CEMENT.



SAMPLER.



MODERN TWENTIETH TWENTYING MACHINE.



OLD FORM OR CYLINDER PRINTING MACHINE.

is

— 1881 — 1882 — 1883 —

70

4

122631

C
R8884kx
"Royal, Institute of Chemistry of Great Britain and
Ireland. Lectures. No. 1.
(Blount Lectures on cement)

DATE.

NAME OF BORROWER

UNIVERSITY OF TORONTO
LIBRARY

[No. 1]

Do not
remove
the card
from this
Pocket.

Acme Library Card Pocket
Under Pat. "Ref. Index File."
Made by LIBRARY BUREAU

